

Exact Results for the Lower Critical Solution Temperature in an Asymmetric Model of an Interacting Binary Mixture

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We have obtained exact results for the lower critical solution temperature (LCST) in a two-dimensional lattice model of an asymmetric binary mixture of large and small molecules (squares *A* and triangles *B*, respectively) in which both couplings ϵ_{AA} and ϵ_{AB} are present. We find that for a LCST to exist in addition to the upper critical solution temperature it is required that the free volume be nonzero, the Flory-Huggins coupling parameter $\chi \equiv \frac{1}{7}(\epsilon_{AB} - \frac{1}{2}\epsilon_{AA})$ be positive, and that $-\epsilon_{AA}$ be much larger than χT . The last two conditions imply that both ϵ_{AA} and ϵ_{AB} must be negative.

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The phase separation that occurs on cooling a binary mixture is readily understood in terms of the reduction of the entropic component of the free energy. This leaves the enthalpic component caused by attractive or repulsive forces between the constituents as the major thermodynamic influence, and phase separation can occur at the upper critical solution temperature (UCST) [1–3]. In polymer blends, however, phase separation may also occur on heating a binary mixture to its lower critical solution temperature (LCST) [4,5]. This phenomenon is less easily understood, as it runs counter to immediate intuition. Theoretical demonstrations of the existence of a LCST have been given within mean-field models [6–10] using the equation-of-state analysis developed by Flory [2] and by Sanchez and co-workers [7,9]. This approach is based on the formulation of an equation relating the pressure, volume, and temperature, and indicates the importance of the compressibility and the free volume of the system. The limits of validity of the mean-field approach have been discussed by Lifschitz, Dudowicz, and Freed [11], who have used the lattice cluster theory to calculate numerically the phase diagrams of specific materials.

In this Letter we present for the first time an exact solution of the phase separation problem in a model that goes beyond the mean-field approximation and which exhibits a LCST. The importance of this calculation lies in the fact that the conditions on the enthalpic contributions necessary for phase separation are clearly demonstrated.

Our model is a variation of that used by Frenkel and Louis [12] in their demonstration of phase separation in a hard-core mixture, and has been used previously in an exact study of the UCST in an asymmetric binary mixture [13]. We consider a mixture of large molecules *A* (black squares) and small molecules *B* (shaded triangles) on a two-dimensional square lattice as shown in Fig. 1. Each black square is allowed to occupy any of the squares on the lattice, the chemical potential is μ_A for this species, and the nearest-neighbor coupling within the species is ϵ_{AA} . Multiple occupancy by the black squares is forbidden. Each unoccupied square on the lattice is then further divided into four triangles. Each of these triangles can be occupied by at most one small particle *B* (the shaded triangles) with a fugacity z_B , and there is no energy cost for contact between shaded triangles. A coupling, ϵ_{AB} , between the small and large molecules is introduced for each edge contact between the black squares and the shaded triangles. Energy costs for point contact between the squares and the triangles are neglected. This model can be thought of in terms of a mixture of monomers (triangles) and oligomers (squares consisting of four tightly bound triangles) with a degree of polymerization of four. The difference between our model and that of Frenkel and Louis [12] lies in the size and shape of molecules *B* (triangles rather than diamonds consisting of pairs of bonded triangles) and the presence of the *A-B* interaction. We will see that the latter is of crucial importance in finding the LCST.

We now briefly describe the thermodynamics of the model. The partition function for the mixture is given by [13]

$$\Xi_{\text{mixture}} = (1 + z_B)^{4N} \sum_{\{n_i\}} \exp \left\{ [-\beta \epsilon_{AA} + 2 \ln(1 + z_B) - 2 \ln(1 + z_B e^{-\beta \epsilon_{AB}})] \sum_{(i,j)} n_i n_j \right\} \\ \times \exp \left\{ [\beta \mu_A - 8 \ln(1 + z_B) + 4 \ln(1 + z_B e^{-\beta \epsilon_{AB}})] \sum_i n_i \right\}, \quad (1)$$

where β is the inverse temperature, n_i takes the value zero (unoccupied) or one (occupied) and thus describes the occupancy of the square at position *i*, and the sum is over all the possible occupation configurations.

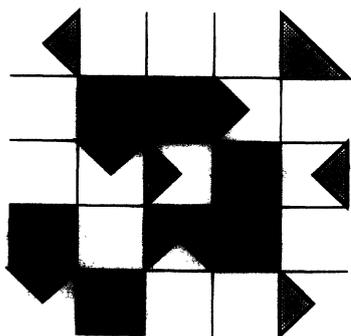


FIG. 1. A phase-separation lattice model for a mixture of large molecules A (black squares) and small molecules B (shaded triangles).

By means of the transformation $n_i = (s_i + 1)/2$, the above partition function is mapped into the partition function of the two-dimensional Ising model with coupling

$$K \equiv \beta J = \frac{1}{2} \ln \frac{1 + z_B}{1 + z_B e^{-\beta \epsilon_{AB}}} - \frac{1}{4} \beta \epsilon_{AA}. \quad (2)$$

and external field $h \equiv \beta H = \frac{1}{2} \ln [z_A / (1 + z_B)^4] - \beta \epsilon_{AA}$, where $z_A \equiv \exp(\beta \mu_A)$ is the fugacity of the large particles. The coexistence curves can be obtained from the exact solution [14–16] of the two-dimensional Ising model with no external field, as was done in Ref. [12]. Along the coexistence curves, the two fugacities thus obey the relation $z_A = (1 + z_B)^4 e^{2\beta \epsilon_{AA}}$. For squares of unit area, we find the number density n_A of large molecules, defined as $\sum_i n_i / N$, to be

$$n_A = \frac{m_{2D} + 1}{2}, \quad (3)$$

and the number density of small molecules to be

$$\begin{aligned} n_B &= \frac{z_B}{N} \frac{\partial \ln \Xi_{\text{mixture}}}{\partial z_B} \\ &= \left(\frac{z_B}{1 + z_B} + \frac{\theta z_B}{1 + \theta z_B} \right) - \frac{1}{2} \left(\frac{z_B}{1 + z_B} - \frac{\theta z_B}{1 + \theta z_B} \right) u_{2D} \\ &\quad - \frac{2z_B}{1 + z_B} m_{2D}, \end{aligned} \quad (4)$$

where $\theta \equiv e^{-\beta \epsilon_{AB}}$, and where u_{2D} and m_{2D} are the energy per site (with J being unity) and spontaneous magnetization per site of the zero-field two-dimensional Ising model, respectively. The molar fraction of the large particles is defined as

$$X_A \equiv \frac{n_A}{n_A + n_B}. \quad (5)$$

The pressure of the system is

$$P = T \left[4 \ln(1 + z_B) - 2K + \frac{1}{N} \ln Z_{2D}(K) \right], \quad (6)$$

where $Z_{2D}(K)$ is the partition function of the two-dimensional square-lattice Ising spin system, and we have set the Boltzmann constant k_B to unity.

To see if there exists a LCST at fixed pressure, the most direct way is to establish the thermal relations along the “surface” of critical points (SCP) and analyze these relations. Since at a critical point $K = K_c \equiv \frac{1}{2} \ln(1 + \sqrt{2})$, we have, from Eq. (2)

$$z_B|_{K=K_c} = \frac{(1 + \sqrt{2})\delta^s - 1}{1 - (1 + \sqrt{2})\delta}, \quad (7)$$

where $\delta \equiv e^{-\chi}$, s is defined as $-\epsilon_{AA}/(2\epsilon_{AB} - \epsilon_{AA})$, and

$$\chi \equiv \frac{1}{T} \left(\epsilon_{AB} - \frac{1}{2} \epsilon_{AA} \right) \quad (8)$$

is the Flory-Huggins coupling parameter. Thus, along the SCP, the pressure is given by

$$\frac{P_c}{\chi T} = -\frac{1}{\ln \delta} \left[4 \ln \frac{\delta(\delta^{s-1}) - 1}{1 - (1 + \sqrt{2})\delta} + C \right], \quad (9)$$

where $C \equiv 6K_c + \frac{1}{N} \ln Z_{2D}(K_c) = 3.57382$ is a constant. We note that for a given pressure P_c , the left-hand side of the above equation is a constant independent of temperature, while the right-hand side is a function only of δ and s . We denote this function as $g(\delta, s)$. The existence of a LCST in addition to an UCST at a fixed pressure then requires $g(\delta, s)$ to be a nonmonotonic function of δ for a given s and within the physically meaningful parameter space (i.e., $z_B \geq 0$, and $\delta \geq 0$). Since at a critical point $m_{2D} = 0$ and $u_{2D} = -\sqrt{2}$, the molar fraction of large molecules is

$$X_A|_{K=K_c} = \frac{1}{1 + (2 + \sqrt{2}) \frac{z_B}{1 + z_B} + (2 - \sqrt{2}) \frac{\theta z_B}{1 + \theta z_B}}, \quad (10)$$

where z_B and θ satisfied Eq. (7).

Having established these thermal relations, we are now in a position to find criteria for the existence of a LCST. Our parameter space (δ, s) lies in $([0, +\infty), (-\infty, +\infty))$. First, we consider three cases which cannot be covered by Eq. (9). (i) For an incompressible system, the fugacity z_B is infinite. From Eqs. (3) and (4) we see that when $z_B \rightarrow \infty$, $n_A + n_B/4 \rightarrow 1$, as was expected for an incompressible system. In this case, we have $\chi = 2K_c$, and thus δ is constant along the SCP. There is only one critical temperature, and this corresponds to the UCST, there being no LCST for the incompressible system. (ii) Consider the case $\epsilon_{AB} = 0$, which implies that there is no interaction between the small and large molecules. This corresponds to $s = 1$. From Eq. (2), we have $\chi = 2K_c$ along the SCP, yielding the same conclusion as in the incompressible case. This shows the important role of a nonzero coupling ϵ_{AB} . In Frenkel and Louis's model, it is not possible to introduce a nonzero ϵ_{AB} , and so it is correspondingly not possible to realize the existence of a LCST. (iii) Here we set the Flory-Huggins coupling χ equal to zero. From Eq. (2) we then find $z_B|_{K=K_c} = [1 - (1 + \sqrt{2})e^{\beta \epsilon_{AA}/2}]/\sqrt{2}$. By

placing this into Eq. (6), one can verify that the pressure is a monotonic function of β along the SCP and within the physically meaningful region, and so this case is excluded as well. More generally, for any given s with $s < 1$ (including negative values), we can show that $g(\delta, s)$ is a monotonic function of δ within the restricted region.

This leaves us with $s > 1$ as the only possible region for finding a LCST. Further examination shows that this is indeed the case. For sufficiently large values of s ($s > s_0$ where s_0 is about 7.5), we have found nonmonotonic behavior of $g(\delta, s)$ as a function of δ . We also have a requirement from the physical constraint $z_B \geq 0$ that χ be positive. We have plotted P_c as a function of δ for $s = 10$ in Fig. 2. From this figure we may deduce the following: When the system is at a fixed high pressure $P > P_u$, there is only a single critical temperature, which corresponds to the UCST. The coexistence curve in δ - X_A space will be essentially the same as that in Ref. [13]. When the pressure is decreased just below P_u , a pair of new critical points emerges. A further decrease in pressure will separate the two critical points, creating an island within which the system is phase separated. Of these two critical points, the one at larger δ becomes a new UCST, while the other becomes a LCST. With further reduction in pressure the old UCST and the LCST converge, and finally coalesce at a pressure P_l , disappearing when the pressure is below P_l . This results in a joining of the two phase-separation zones into a single indented (i.e., hour-glass shaped) region. To confirm our analysis we have plotted the coexistence curves in the δ - X_A plane for various pressures at $s = 10$. Indeed, for $P > P_u$, the phase diagram is simple. For $P = 10$, which lies between P_u and P_l , the phase diagram is as shown in Fig. 3. One can observe two separate phase-separation zones and the existence of a LCST. For $P = 8$, which is below P_l , the phase diagram is as shown in Fig. 4. The indented shape of the phase boundary implies that phase separation by heating can occur even without a LCST. Because s_0 is much larger than one and χ is positive, both the couplings

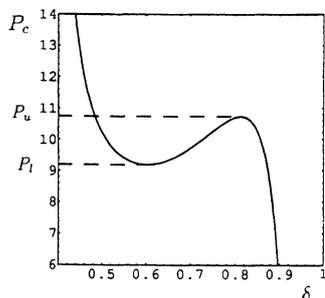


FIG. 2. This shows the pressure P_c at the critical point as a function of the temperature-dependent parameter δ . Here $s = 10$ (i.e., $\epsilon_{AB} = 0.45\epsilon_{AA}$) and units have been chosen such that $\chi T = 1$.

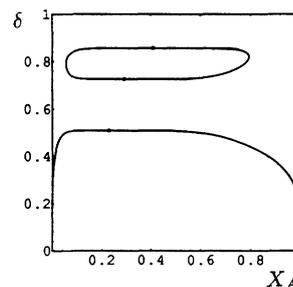


FIG. 3. This illustrates the coexistence curves at a constant pressure $P/\chi T = 10$ in the δ - X_A phase plane, where X_A is the molar fraction of molecules A and δ is related to temperature. The dots represent the critical points and can be found from Eqs. (8) and (10).

ϵ_{AA} and ϵ_{BB} must be negative in order to find a LCST in this model.

The qualitative physical picture behind this analysis can be described in terms of the effect of free volume. A large value of s indicates that either $-\epsilon_{AA}$ is relatively large or that χT is relatively small. Let us look at the region in Fig. 3 where $P_l < P < P_u$. At low temperatures, there is very little free volume, and the entropy plays no role. Each molecule A is thus in contact with another molecule of either type A or type B . The effective coupling ϵ_{eff} will be χT , and if χ is positive the mixture phase separates. When the temperature is increased, the free volume increases and the entropy becomes more important. If χ is small, the increasing entropy will terminate the phase separation of the mixture at a relatively low temperature (UCST) before the free volume has any significant effect on the mixture. When the temperature is raised further, the free volume increases. Now, since there is a significant amount of free volume, each molecule may be in contact with another molecule A , a molecule B , or empty space, and the effective coupling is no longer χT . In comparison with incompressible mixtures, the free volume affects the mixture in two ways. On the one hand, it raises the energy of those configurations which favor a disordered phase because of the negative value of ϵ_{AB} . On the other hand, it can significantly raise the entropy of the phase-separated configurations without much increasing their energy since ϵ_{AA} is also negative. If $-\epsilon_{AA}$ is large enough, and the temperature, which is above the UCST, is not too large, the phase of the mixture can be determined, again, by those configurations that favor phase separation. At very high temperatures, there is now too much free volume, and there are few contacts between molecules. Consequently, entropy takes over, changing the mixture back into the disordered phase. For $P > P_u$, the increase with temperature of the free volume slows down, and so its effect is suppressed. For $P < P_l$, the free volume can cause effects even within the two-phase region, resulting in the indented shape of the coexistence curve shown

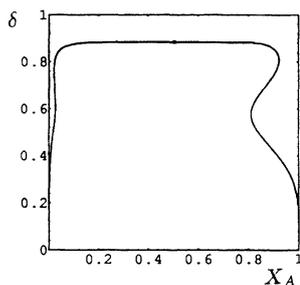


FIG. 4. This illustrates the coexistence curves at a constant pressure $P/\chi T = 8$ in the δ - X_A phase plane. The dot represents the single critical point.

in Fig. 4. In this example, a solution of molar fraction $X_A = 0.9$ will show phase separation upon increase of temperature.

A comparison of these conclusions may be made with those of a recent mean-field calculation for blends of diblock copolymers due to Yeung *et al.* [10]. These workers chose the parameters χ to be positive and $\Sigma \equiv -(\chi_{AA} + 2\chi_{AB})/2$ to be much larger than χ in order to conform with the experimental results of Russell *et al.* [5]. Their calculation thus concerns a regime for which in our notation $s \gg s_0$. Their finding of the possibility of phase separation upon heating within their mean-field model is thus not unexpected from the viewpoint of the exact solution of our rather different model. One should, however, be careful to draw a distinction between the mere phenomenon of phase separation upon heating and the existence of a LCST. An hourglass-shaped coexistence curve of the type shown in Fig. 4 can give rise to the former process without exhibiting any LCST.

In conclusion, we have found an exact solution for a two-dimensional lattice model of an asymmetric binary mixture that exhibits a LCST in addition to an UCST

at fixed pressure. We have established criteria for the existence of this phenomenon, and describe it in terms of the effects of free volume. These criteria should be helpful in more general studies of the formation of a LCST. We have also pointed out that the occurrence of phase separation induced by heating does not necessarily imply the existence of a LCST.

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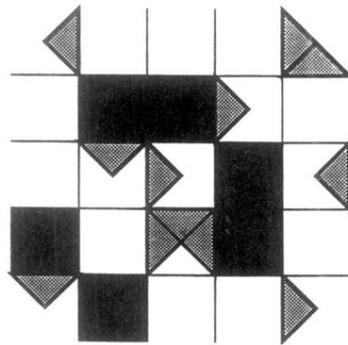


FIG. 1. A phase-separation lattice model for a mixture of large molecules *A* (black squares) and small molecules *B* (shaded triangles).